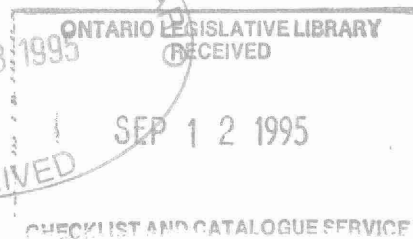


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**PILOT STUDY FOR THE DEVELOPMENT OF A
BIOLOGICAL REFERENCE MATERIAL FOR
ORGANOCHLORINE CONTAMINANTS**

Final Report of RAC Project No. ER 570C

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Laboratory Services Branch
Ontario Ministry of the Environment

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Summary

Results of this study show that a homogeneous and stable biological material suitable for use as a certified reference material for polychlorinated biphenyls, dibenzo-p-dioxin and dibenzofurans can be produced. The pilot material is whole carp harvested from Saginaw Bay, Lake Huron, that has been processed into a slurry and sealed as approximately nine gram quantities in glass ampoules. The concentrations of major polychlorinated biphenyl congeners in this material have been shown to remain constant at room temperature for a period of at least five months. Similar materials have been stored unchanged with respect to trace element contents for at least five years.

Introduction

Organochlorine compounds have aroused much interest amongst environmental and analytical chemists in the last two decades. Of these, three classes of compounds, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) have received the most attention because of their ubiquitous presence in the environment, their anthropogenic origin, and their assumed toxicity. One of the PCDD congeners, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, has been labelled as "the most toxic man-made chemical" [1]. PCBs are generally regarded as less toxic; past accidental poisonings involving PCBs have been attributed to PCDFs present as impurities [2]. The general perception of PCB toxicity may need reconsideration in view of the recent discovery of highly toxic coplanar congeners, such as 3,3',4,4'-tetrachlorobiphenyl, 3,3',4,4',5-pentachlorobiphenyl and 3,3',4,4',5,5'-hexachlorobiphenyl, that have been demonstrated to be present in significant quantities in commercial PCB mixtures and biological tissues [3-6]. Recent analyses of Japanese adipose tissues indicate that coplanar PCB concentrations are about ten times higher than those of PCDDs and PCDFs. This has led some to believe that coplanar PCBs may pose a greater toxic threat than PCDDs and PCDFs to humans as well as to wildlife [3,6,7].

One of the most important aspects of method development and quality assurance of analytical results is validation by means of certified reference materials (CRMs). The essential requirements [8] of a CRM are that it be (a) representative of the real analytical problem inasmuch as it presents a similar matrix and comparable analyte load; (b) stable with respect to

the analyte and the matrix; (c) homogeneous; (d) accurately certified. The need for CRMs is, perhaps, best reflected by the general lack of comparability exhibited in results of interlaboratory comparisons [e.g., 9]. Despite the important role CRMs play and the immense environmental impact of organochlorine compounds, very few CRMs for organochlorine pollutants exist. This acute shortage is exacerbated by the fact that the few available CRMs are all of a single type, sediment, and are certified for a single type of compounds, the PCBs. A frozen mussel tissue reference material that carries "non-certified concentrations" for 13 PCB congeners has recently become available from the U.S. National Institute of Standards and Technology [10]. However, to date, no biological tissues certified for PCBs, PCDDs or PCDFs exist. This lack of biological CRMs is especially unfortunate since most monitoring for organochlorine compounds involves biological tissues. From a CRM developer's point of view, this phenomenon is understandable considering the relative difficulties involved in producing a sediment and a biological CRM for organochlorine compounds. As well, it is not surprising that no CRM for PCDDs and PCDFs exists because of the difficulties faced and skills required in their certification.

This report describes the results of a pilot study for the development of a biological CRM for PCBs, PCDDs and PCDFs, which was funded partially by the Ontario Ministry of the Environment.

Preparation of the Prototype CRM

Choice of Material

The biological tissue appropriate for this study must satisfy several criteria: (a) it must contain PCBs, PCDDs and PCDFs; (b) it must be available in kilogram quantities; (c) similar materials and quantities must be available in years to come. As well, the organochlorine concentrations should be relatively high so as to render this material useful to as many laboratories as possible.

After much consultation with experts in the Ontario Ministry of the Environment, Health and Welfare Canada, and Fisheries and Oceans Canada, ground whole carp from Lake Huron was chosen as the material for this pilot study. The carp sample was harvested from Saginaw Bay in Lake Huron near the warm water discharge of the Consumer's Power Plant on December 2, 1988, ground whole and stored at -20°C . An approximately 30-kg sample was made available to us courtesy of the U.S. Fish and Wildlife Service in East Lansing, Michigan. The carp population in Saginaw Bay is large and stable, and should allow future repetitive sampling on this scale.

Portions of the carp material have been examined by various laboratories, including the Canadian Wildlife Service, Environment Canada, and were found to contain relatively high concentrations of organochlorine contaminants. A 49-g sample of the portion received by the Canadian Wildlife Service was made available to us for testing.

Preliminary Investigations

Our experience in processing biological tissues for use as CRMs led us to decide that the aqueous slurry approach pioneered by this laboratory would carry a lower risk of failure than the more common freeze-drying approach. The lipid content of the carp tissue would likely be

too high and would render any freeze-dried material a "peanut-butter" type texture, which would present difficulties in further handling.

The Canadian Institute of Fisheries Technology, Technical University of Nova Scotia handled pilot processing of the carp material. Approximately 1 kg of tissue was chopped from the frozen 30-kg batch, allowed to thaw and processed in a food cutter (Comitrol, Model 3600, Urschel Laboratories Inc., Valparaiso, IN) equipped with a fine Type K 28 column 015-030 cutter. (The first number in the cutter designation refers to the measurement in thousandths of an inch of the width of the cutter knives and the second to the separation between the knives.) After one pass, 850 g of distilled water and 0.42 g of an antioxidant (ethoxyquin powder) was mixed with 850 g of tissue and processed again in the food cutter. This slurry was then heated to 80°C, processed a third time and deaired under vacuum. The moisture content of this material was found to be 83%.

Portions of this slurry were diluted with various amounts of distilled water to achieve moisture contents in the range from 83 to 88%, placed in ampoules and thermally processed in a steam retort at a target temperature of 118°C and a process lethality $F_0 = 6$ min. This process has an equivalent effect on bacterial destruction as heating instantaneously to 121°C and holding for 6 min. Slurries containing higher percentages of water were found to be less prone to separate into two phases and have a consistency more acceptable with respect to further processing. The sealed ampoules were shipped to the Institute for Environmental Chemistry, National Research Council (NRC) for evaluation and PCB determination (see later sections for details). It was decided that the optimal water content to be used in the production work would be 85%. This percentage would minimize the amount of water added to the slurry while

maintaining an acceptable fluid behaviour.

Production Procedures

The remainder of the frozen carp was removed from cold storage (at $\approx -30^{\circ}\text{C}$) and thawed overnight at room temperature. This tissue was first comminuted four times using the food cutter equipped with a Type K 28 column 010-020 cutter on the first pass and a finer 010-010 cutter on subsequent passes. After the first pass, the weight of raw material was reduced to approximately 16 kg. 9.5 g of an antioxidant, ethoxyquin powder, was added to the material. The moisture content was determined (by means of a moisture balance, Ohaus Scale Corp., Model 6010, Union, NJ) to be 62%. Distilled water was added to bring the moisture content to 85%.

The resulting slurry was processed four times in a homogenizer (No-Bac Unitherm IV, Cherry-Burrell Corp., Cedar Rapids, IO) at pump/homogenizing valve pressures of 2100/2600, 2500/3000, 2500/4000, and 2500/4000 psi on progressive passes. After homogenization, the slurry was divided and bottled by means of an ampouling machine (Cozzoli Machine Co., Plainfield, NJ). The machine cycle consisted of four operations: nitrogen flushing the empty ampoule, filling the ampoule with a metered volume of homogenate, nitrogen flushing the headspace, and finally sealing the ampoule with a propane/oxygen flame. The machine had been calibrated using distilled water to deliver 10 mL.

To stabilize the sealed homogenate, the ampoules were thermally processed in a steam retort (WSF Industries Inc., Tonawanda, NY) at 118°C for 11 min. This thermal process achieved lethalties, F_0 , between 6.0 and 6.6 min. After cooling, the ampoules were inspected

for closure integrity, and heat-sealed in individual 100 x 127 mm trilaminate retort pouches (Reynolds Metals Co., Richmond, VA). The pouches were packed with foam chips, in corrugated paperboard cartons, and shipped to NRC.

Analytical Results

After receipt of the pilot CRM material in Ottawa, 200 ampoules were selected for various analyses. The remaining ampoules were placed in storage at room temperature. The ampoules earmarked for analysis were also stored under similar conditions until use.

The ampouled carp slurry has a texture and consistency similar to those of a lobster hepatopancreas slurry which we previously processed. On standing, the slurry separates into a solid and a liquid phase, which can easily be re-homogenized by means of sonication. Portions of a re-homogenized slurry may be sampled for analysis, if necessary.

The homogeneity and stability of the carp tissue were examined by means of PCB determination.

Determination of PCBs

The following is a brief description of the extraction, clean up and analytical techniques employed for PCB determination. All chemicals were reagent grade or better. Solvents were all distilled-in-glass grade. The content of an ampoule was sonicated for 2 minutes and mixed with a sufficient quantity (about 46 g) of anhydrous sodium sulphate (previously heated to 450°C) to attain a free-flowing state. The mixture was extracted for seven hours in a Soxhlet

apparatus using 175 mL of 1/1 acetone/hexane. The extract was reduced to a few mL by means of rotary evaporation.

Twenty grams of Florisil, 60-100 mesh (Supelco Inc.), deactivated with 2% water, was packed in a 50-mL buret. The extract was transferred to the Florisil column. The PCBs were eluted with 300 mL of hexane. The hexane solution was evaporated down to 1 mL for clean up on an alumina column. A 3.7-g sample of activated alumina F1 (Chromatographic Specialties Inc.), 40/60 mesh, was packed into a 10- mL borosilicate glass serological pipet, followed by a thin layer of anhydrous sodium sulphate. The column was then activated at 190°C for 2 days. The concentrated hexane extract was applied to the alumina column. The column was washed with 10 mL of hexane. The PCBs were then eluted with 50 mL of 15% ethyl ether in hexane. The volume was reduced to 0.5 mL. This solution was transferred to a 2-mL volumetric flask. The appropriate amount of CB-194 was added as internal standard, and hexane was added to the mark. Concentrations of PCB in this solution were appropriate for mass spectrometric examination, which was sometimes carried out.

The bulk of the assessment work, however, was carried out using gas chromatography with electron capture detection (GC-ECD). For this technique, the 2-mL hexane solution was diluted ten fold prior to injection. This ensured that the PCB concentrations lay within the linear response range of the electron capture detector.

Determination of PCDDs and PCDFs

The organochlorine compounds were removed from the carp tissue by Soxhlet extraction as detailed above. The clean-up procedure was a modified version of one developed by Ryan

et al. [11], which involved defatting with sulphuric acid and multi-column clean up in the following order, acid and base impregnated silica gel, Florisil, and carbon.

The carp tissue was spiked with the appropriate amounts of ^{13}C -labelled PCDD and PCDF congeners, including 2,3,7,8-tetra-, 1,2,3,7,8-penta-, 1,2,3,4,7,8-hexa-, 1,2,3,6,7,8-hexa-, 1,2,3,7,8,9-hexa-, 1,2,3,4,6,7,8-hepta-, and octachlorodibenzo-p-dioxin, as well as 2,3,7,8-tetra- and 1,2,3,7,8-pentachlorodibenzofuran, prior to extraction. Acetone from the Soxhlet extract was removed by means of partitioning with 40 mL of water. The hexane phase was removed. The aqueous phase was washed with 50 mL of hexane. The hexane solutions were then combined and washed for the last time with 30 mL of water. To dry the hexane solution, it was passed through a filter paper containing a little anhydrous sodium sulphate on top. The filtrate was collected in a 100-mL volumetric flask. The filter paper was then washed with hexane to bring the final filtrate volume to 100 mL.

A 10-mL portion of this solution was sometimes removed for lipid measurement. The remaining portion was transferred to a 250-mL separatory funnel, followed by 60 mL of hexane. Twenty millilitres of concentrated sulphuric acid was added. After shaking and phase separation, the aqueous phase was removed. This process was repeated 5 to 6 times until the aqueous phase became clear and pale yellow in colour. The defatted hexane solution was then washed successively with 20 mL of water, 20 mL of 1% aqueous potassium hydroxide, and again 20 mL of water. It was then filtered through a Whatman number 1 paper containing a thin layer of anhydrous sodium sulphate, and reduced in volume to about 1 mL via rotary evaporation.

The silica gel column and the Florisil column clean up were run in tandem. Cesium

hydroxide-impregnated silica was prepared as follows: 30 g of cesium hydroxide was dissolved in 100 mL of methanol. This solution was poured into 100 mL of methanol followed by 50 g of activated silica gel, 40-60 mesh (Chromatographic Specialties Inc.). This mixture was allowed to remain at 55°C for 90 min, after which it was filtered. The silica gel was washed with 200 mL of methanol and then with 200 mL of dichloromethane. Sulphuric acid-impregnated silica gel was synthesized by shaking 2 parts of concentrated sulphuric acid with 3 parts of activated silica gel, 40-60 mesh, until the mixture was free of lumps and of a uniform consistency (about 15 min.). Both silica materials were prepared ahead of time and stored in closed jars. However, since these materials deteriorate slowly under laboratory conditions, column packing was performed just prior to use. One gram of the sulphuric acid-, 0.5 g of the cesium hydroxide-impregnated silica gel, and 0.5 cm of anhydrous sodium sulphate were packed, in that order, in a 5-mL serological pipet. The column was first washed with 10 mL of hexane and then mounted on top of a Florisil column.

For the Florisil column, 1.5 g of Florisil, 60-100 mesh, previously extracted with dichloromethane, was packed into a 5-mL pipet followed by a 1-cm layer of anhydrous sodium sulphate. This column was activated at 130°C for 24 hours. Before use, the column was washed with 10 mL dichloromethane followed by 10 mL 2% dichloromethane in hexane. The Florisil column was then coupled to the silica gel column.

The concentrated and defatted hexane solution was applied to the silica gel and Florisil column in tandem. The flask and the columns were then washed with a total of about 15 mL of hexane. The silica gel column was removed. A 20-mL solution of 2% dichloromethane in hexane was used to elute PCBs from the Florisil column. PCDDs and PCDFs were eluted with

50 mL of dichloromethane. The volume of this eluate was reduced. Dichloromethane was replaced with hexane; this solution was ready for carbon clean up.

An adsorbent of 18% Carbopack C, 80-100 mesh (Supelco Inc.), on Celite 545 (Fisher Scientific) was prepared by means of shaking 3.6 g of the carbon with 16.4 g of the diatomaceous earth until a uniform consistency as well as colour was observed. A 0.25-g portion of this material was packed into a 5-mL serological pipet that had previously been packed with 0.2 g of anhydrous sodium sulphate. The column was then washed with 2 mL of toluene, 1 mL of 1/1 cyclohexane/dichloromethane, and 2 mL hexane, in that order, prior to use. The sample was added to the column, followed by 2 mL of hexane and then 1 mL of 1/1 cyclohexane/dichloromethane to elute remaining PCBs and pesticides. Fifteen millilitres of toluene was used to elute PCDDs and PCDFs.

The toluene solution was reduced to 0.5 mL on a rotary evaporator, and further reduced to approximately 100 μ L with the aid of a stream of nitrogen. An appropriate amount of the recovery standard ^{37}Cl -labelled 1,2,3,4-tetrachlorodibenzo-p-dioxin was added. The solution was evaporated down; the solvent was changed to toluene and reduced to 20 μ L. This solution was ready for gas chromatography/high resolution mass spectrometric (GC/HRMS) analysis.

Instrumentation

GC-ECD Measurements were performed on a Varian, Model 3300, gas chromatograph equipped with a split/splitless injector, a 30-m x 0.25-mm ID DB-5 column with 0.25 μ m film thickness (J & W Scientific), and a constant current-variable frequency electron capture detector. Data were handled on a Varian Saturn IBM-PC based integration and data storage system. Some

determinations were also made on a Varian, Model VISTA 6000, gas chromatograph also equipped with a split/splitless injector and a constant current-variable frequency electron capture detector, but with a 30-m x 0.25-mm ID DB-1701 column with 0.25 μ M film thickness (also from J & W Scientific). Data reduction on that system was performed on a Spectra-Physics, Model SP4400, integrator.

GC/HRMS Determinations were conducted on a VG Autospec-Q hybrid mass spectrometer having an EBEqQ geometry. This instrument is capable of unattended automatic runs for a period of days. All measurements were carried out solely by means of the high resolution mode with a typical resolution of 10,000. Sample injections were performed in the splitless mode on a 60-m x 0.25-mm ID DB-5 column with a film thickness of 0.1 μ m (J & W Scientific).

PCB Data

Figure 1 shows a chromatogram of the carp tissue extract obtained on the gas chromatography-electron capture detection system employing a DB-5 column. The peaks that are labelled have retention times that match those congeners. Mass spectrometric examination confirmed that the degrees of chlorination of these (or the major component of these) peaks agree with the congeners labelled. As well, the existence of these congeners in the tissue have also been confirmed on a second, DB-1701 column.

Although we have little doubt that the congeners, CB-101, 118, 153, 138, 187, 180, 170, 199 and 196, are present in the carp material, it is highly likely that some of the peaks that are labelled as such in Figure 1 do contain other congeners (i.e. some of these peaks are likely to

contain two or more congeners unresolved). Some of these unresolved congeners may be injected and separated on a second column of different polarity or separation chemistry in a two-dimensional gas chromatographic run. We are scheduling to have a two-dimensional gas chromatograph installed in our laboratory early 1993 to allow us to separate and quantify individual congeners at a higher degree of confidence. Until this is possible, every congener assignment is tentative and any congener concentration reported (see later sections) should be understood as the total concentration of a particular peak, which may contain several congeners, measured as that congener.

The carp material has been analyzed on a regular basis for the suite of 9 PCB congeners. This is to assess both the homogeneity and the storage stability of the material. Figure 2 shows the measured "congener" concentrations of 8 samples analyzed over a period of 5 months. It is evident that the carp material is homogeneous and stable with respect to room temperature storage. The amount of slurry contained in the vial is 8.91 ± 0.18 g for the 8 samples. The carp material contains relatively high concentrations of PCBs, which may be a desirable feature for a first biological CRM material as it should have as wide an applicability as possible.

PCDD and PCDF Data

The concentrations of priority PCDD and PCDF congeners in the carp tissue are also relatively high. Figures 3 and 4 show selected ion chromatograms of the tetra-, penta-, and hexachlorodibenzo-p-dioxin and -dibenzofuran congeners identified in the carp extract; the two most abundant ions for each level of chlorination are shown. As confirmation analysis is continuing, the congener assignments and concentrations reported here are tentative and may be

revised in the future. Table 1 shows the concentrations of the PCDD and PCDF congeners identified in one typical analysis.

Future Work

It is evident from the results we have so far that the carp material is homogeneous and stable, and contains relatively high concentrations of a suite of PCB, PCDD and PCDF congeners. Aside from the two-dimensional gas chromatographic study that we previously mentioned for PCBs, we also need to confirm the PCDD and PCDF congeners' identification on other types of high resolution columns. Another immediate task that needs pursuing is to have collaborative studies from expert laboratories on the material. The degree of correlation on the analytical data from these laboratories would allow us to judge if certification of the carp tissue with respect to particular organochlorine congeners is possible. We are targeting a completion date of September 30, 1993 for this extension of the current project. As well, the storage study which was initiated in April will continue for at least another year.

Conclusion

Results of this pilot study indicate that a homogeneous and stable slurry suitable as a biological certified reference material for PCBs, PCDDs and PCDFs can be produced and stored under room temperature conditions. Since this material was heat stabilized and sealed in ampoules, it is sterile and is expected to have a shelf-life in terms of years. Our other biological slurry has remained stable with respect to both analyte (trace element) concentrations and matrix

integrity under room temperature storage conditions for a period of five years. It is expected that this material will have at least another five years' of shelf life. We are projecting a similar storage property for the carp tissue. As well, since the material has been heat stabilized, we do not expect possible exposure of the ampoules to elevated temperatures while they are being transported to customer laboratories would cause any premature decomposition. An indirect proof is that, to date, we have not received any notice of decomposition of any of our biological CRM during transit or laboratory storage.

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Table 1

Determination of PCDD and PCDF congeners in the carp tissue

Congener	Concentration (pg/g)
2,3,7,8-TCDF ^a	13.4 $\pm$ 0.3 ^b
2,3,7,8-TCDD	8.2 $\pm$ 1.3
1,2,3,7,8-PeCDF	4.7 $\pm$ 0.4
1,2,3,7,8-PeCDD	4.5 $\pm$ 0.1
1,2,3,4,7,8-HxCDD	1.5 $\pm$ 0.2
1,2,3,6,7,8-HxCDD	6.0 $\pm$ 0.4
1,2,3,7,8,9-HxCDD	0.4 $\pm$ 0.3
1,2,3,4,6,7,8-HpCDD	6.4 $\pm$ 0.6
OCDD	11.5 $\pm$ 0.4

^a CDD, chlorodibenzo-p-dioxin; CDF, chlorodibenzofuran; T, tetra; Pe, penta; Hx, hexa; Hp, hepta; O, octa.

^b Standard deviation of four injections of the same extract.

Figure Legends

- Fig. 1. PCB congeners in the carp material as separated on a DB-5 column. Electron capture detection; peaks that contain tentatively identified congeners are labelled.
- Fig. 2. PCB "congener" concentrations. z-axis is ampoule number. Extract dates (day/month): #39, 6/4; #1, 11/5; #52, 25/5; #97, 9/6; #128, 22/6; #193, 6/8; #195, 19/8; #280, 1/9.
- Fig. 3. Selected ion chromatograms of tetra-, penta- and hexachlorodibenzo-p-dioxin congeners as separated on a DB-5 column. The two most abundant ions for each level of chlorination are shown.
- Fig. 4. Selected ion chromatograms of tetra- and pentachlorodibenzofuran congeners as separated on a DB-5 column. The two most abundant ions for tetra- as well as pentachlorodibenzofuran are shown.

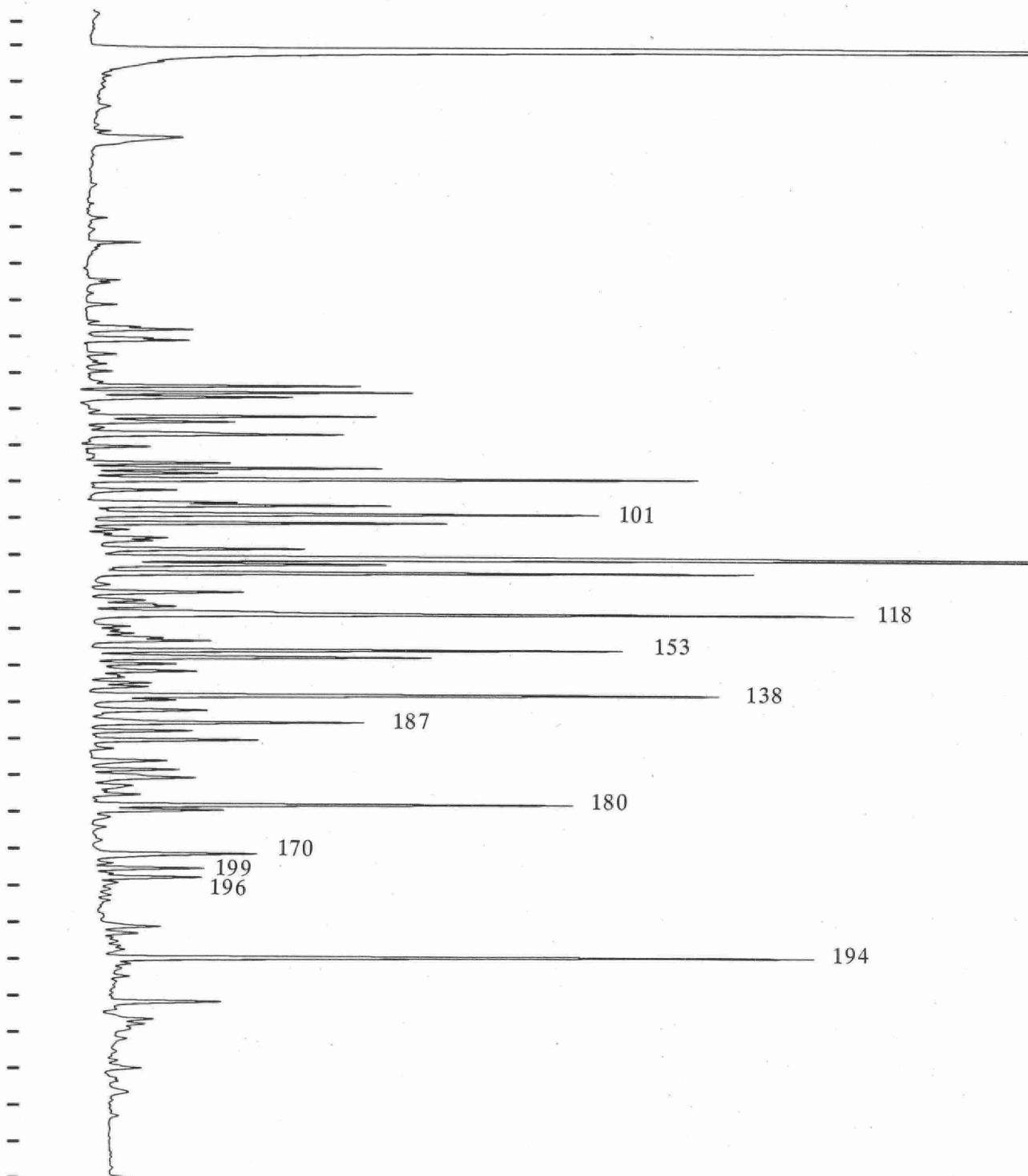
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Workstation: MIKE_1 Bus Address : 16
Instrument : Varian Star #1 Sample Rate : 10.00 Hz
Channel : A = ECD 64 x 10 Run Time : 37.002 min

***** Varian GC Star Workstation ***** Rev. A 05/23/91 *****

Chart Speed = 0.60 cm/min Attenuation = 300 Zero Offset = 5%
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CARP

PCB "congeners"

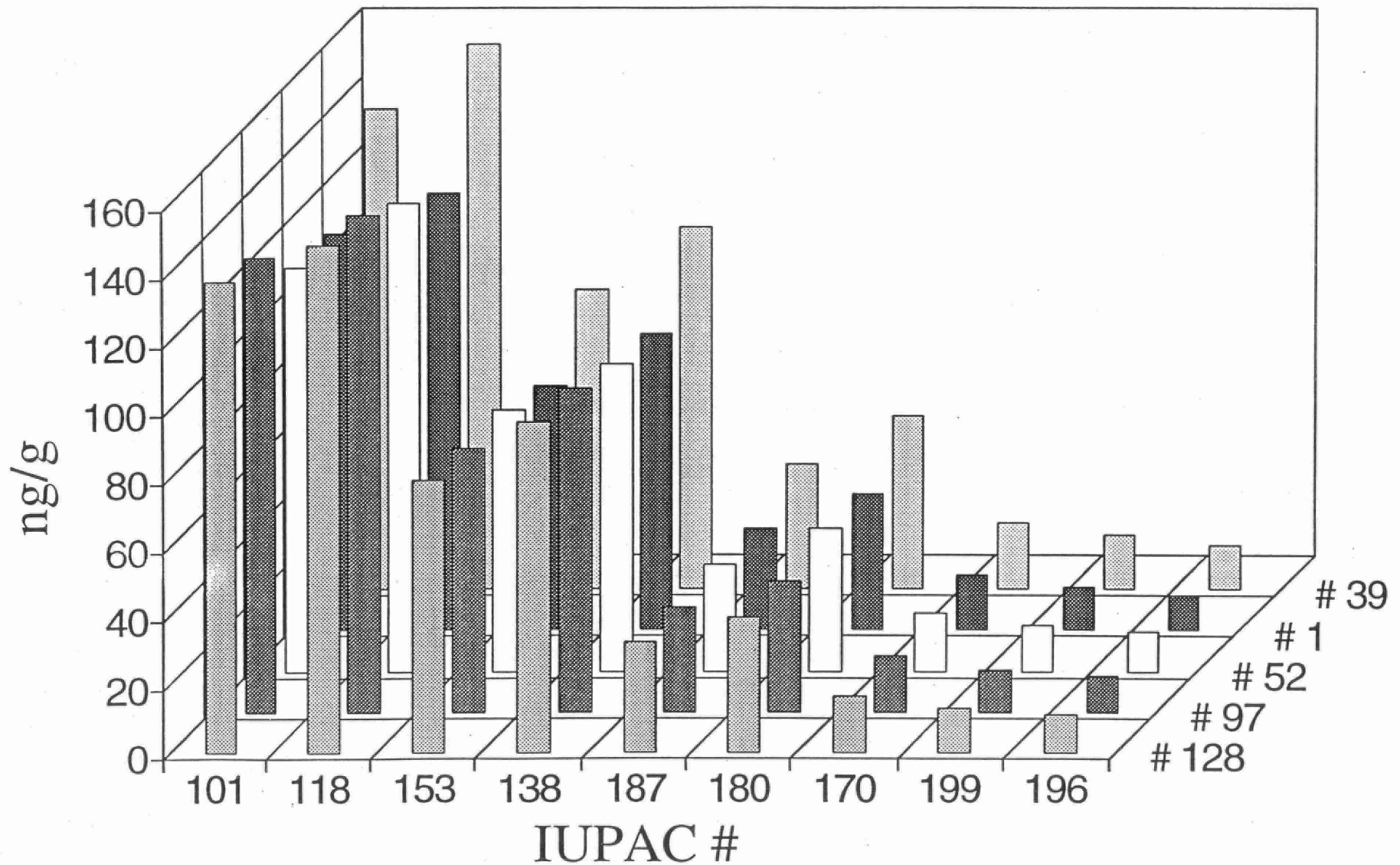
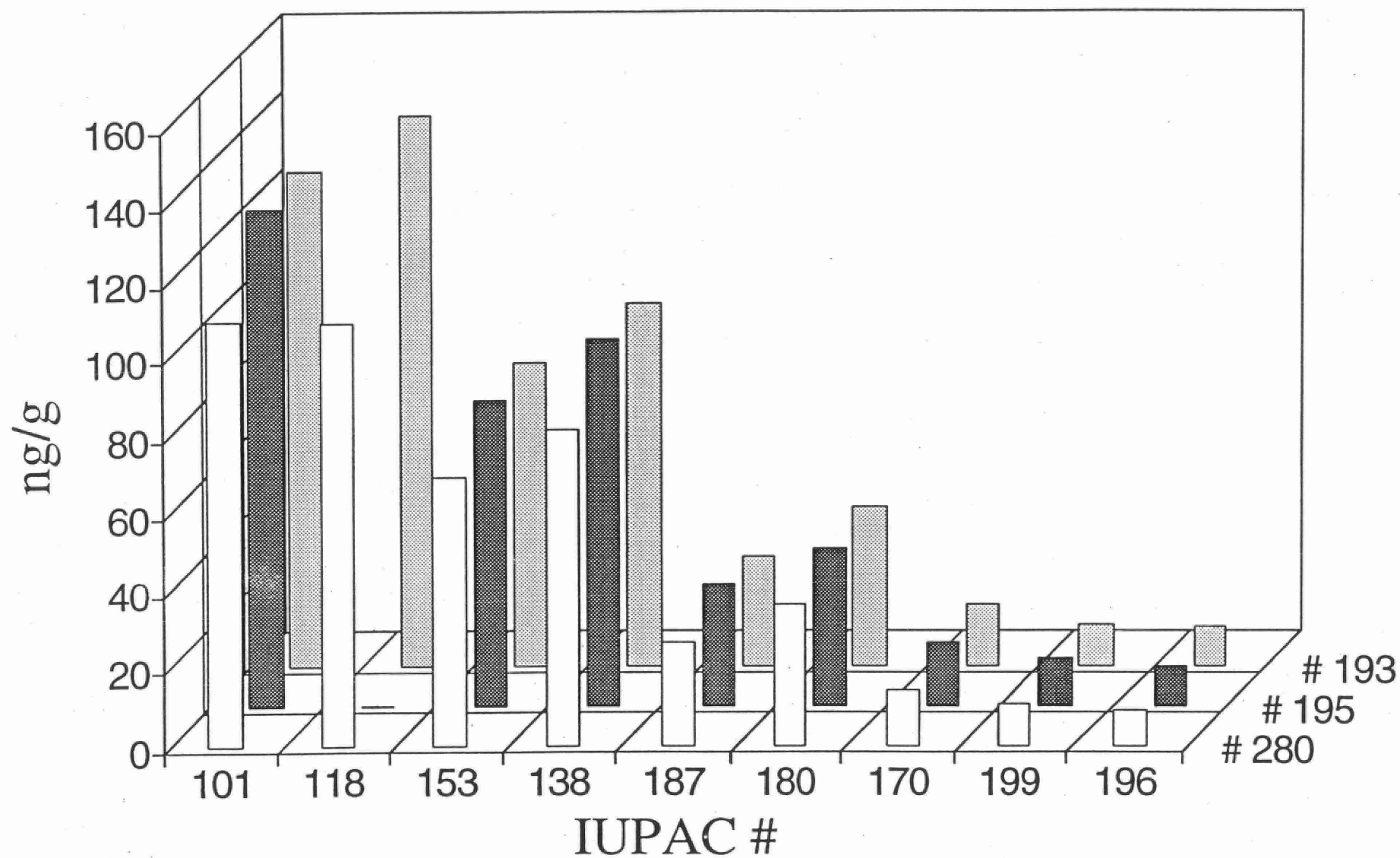
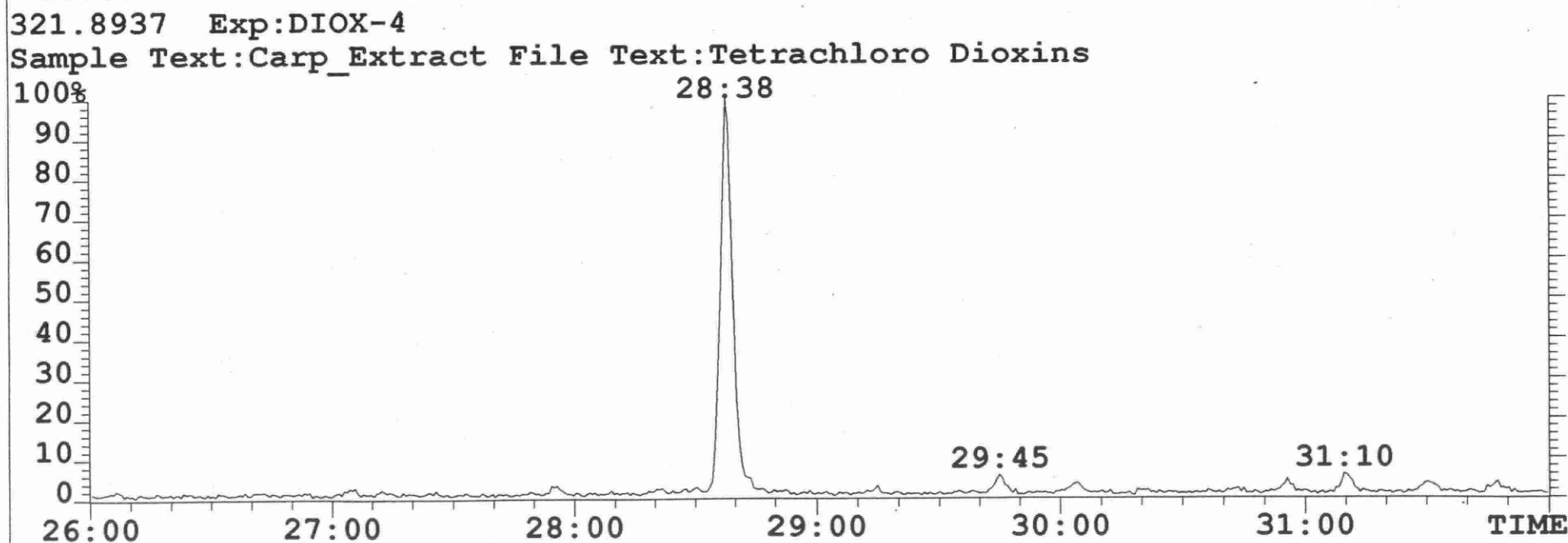
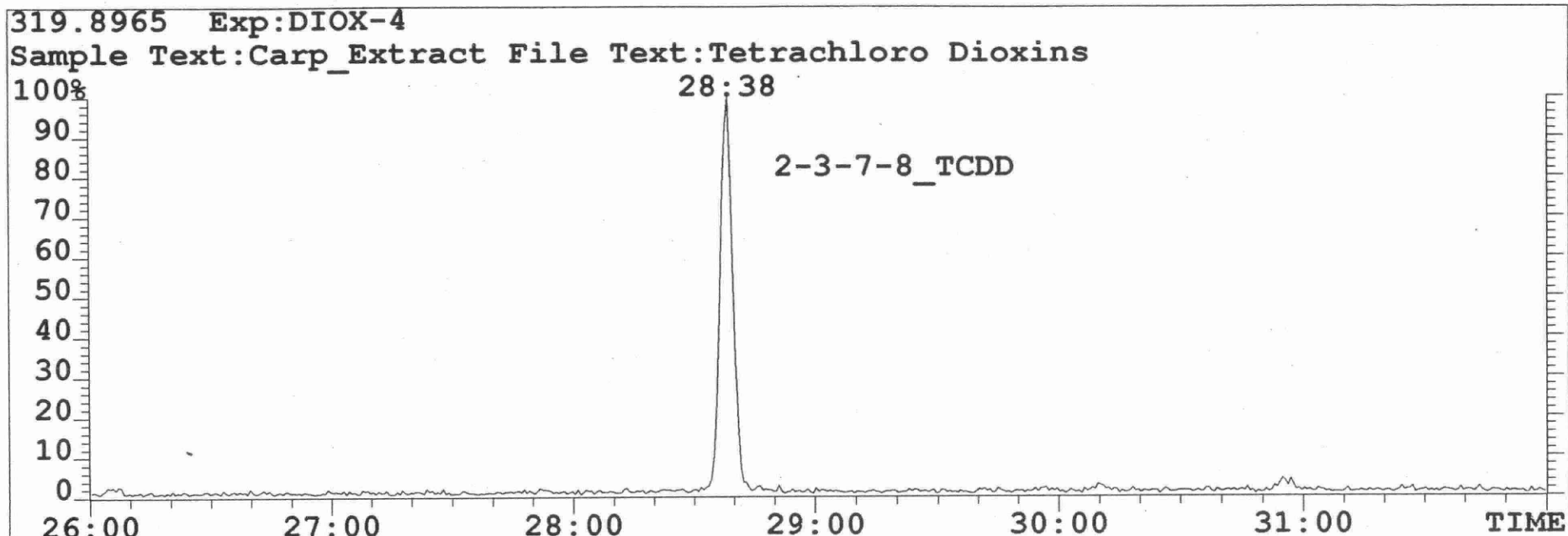


Fig. 2a

CARP

PCB "congeners"





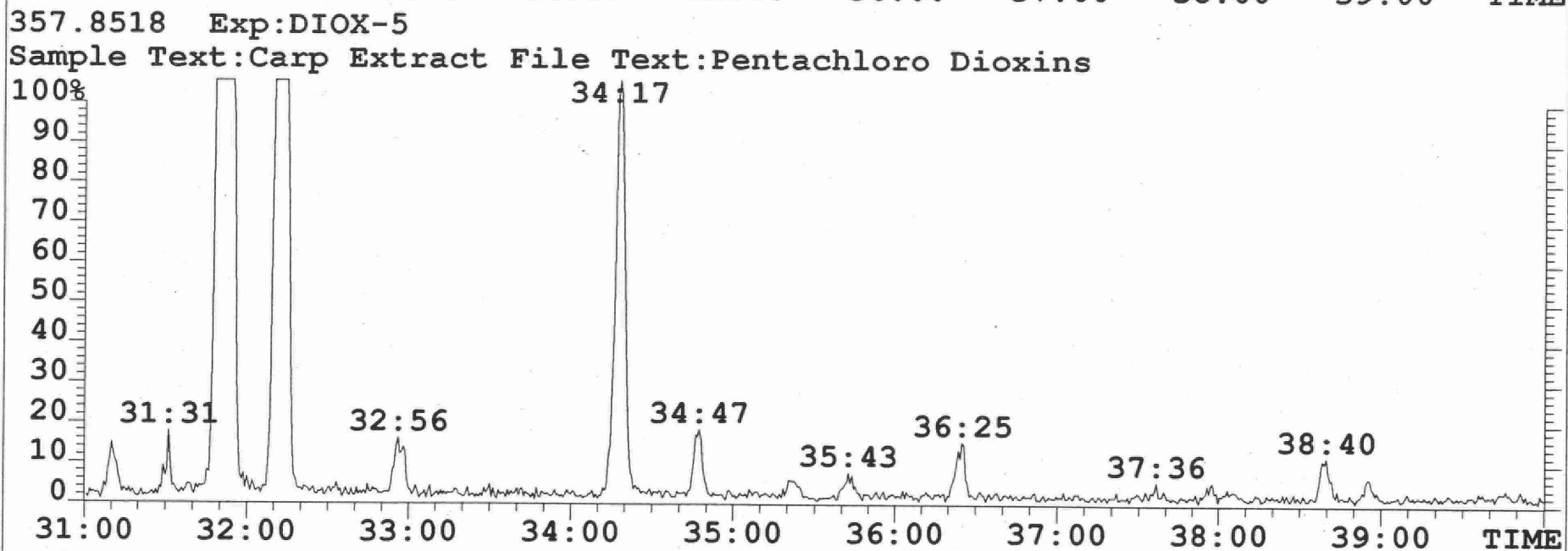
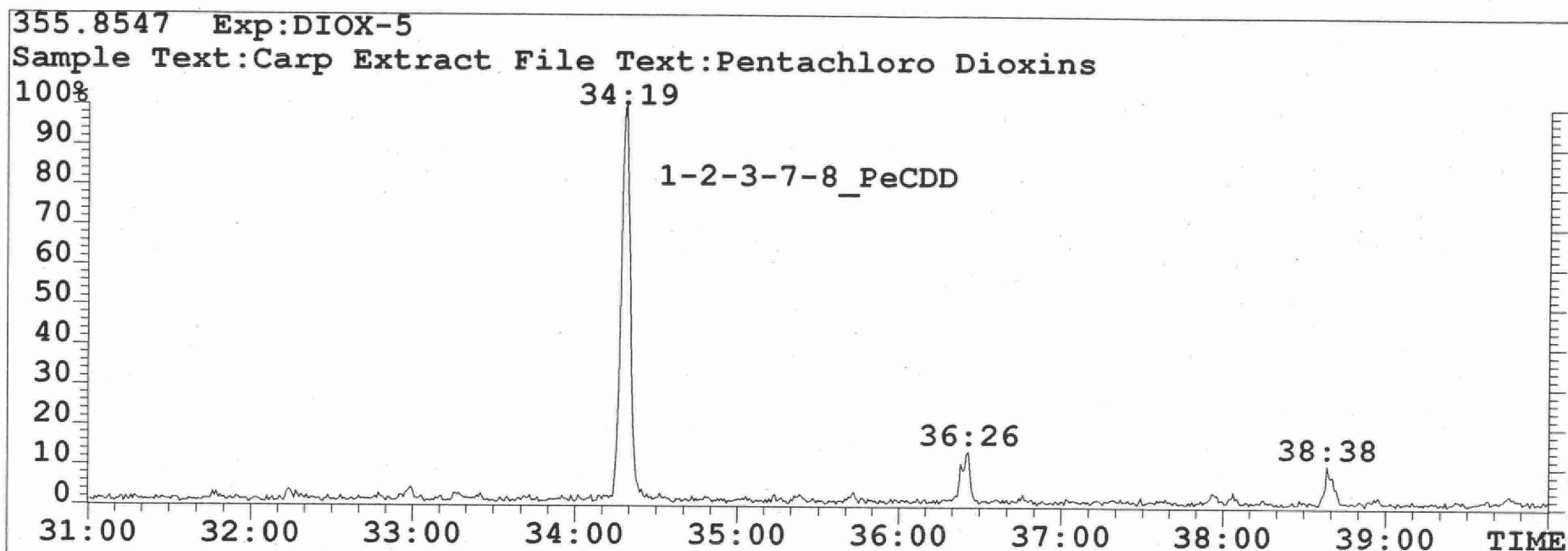
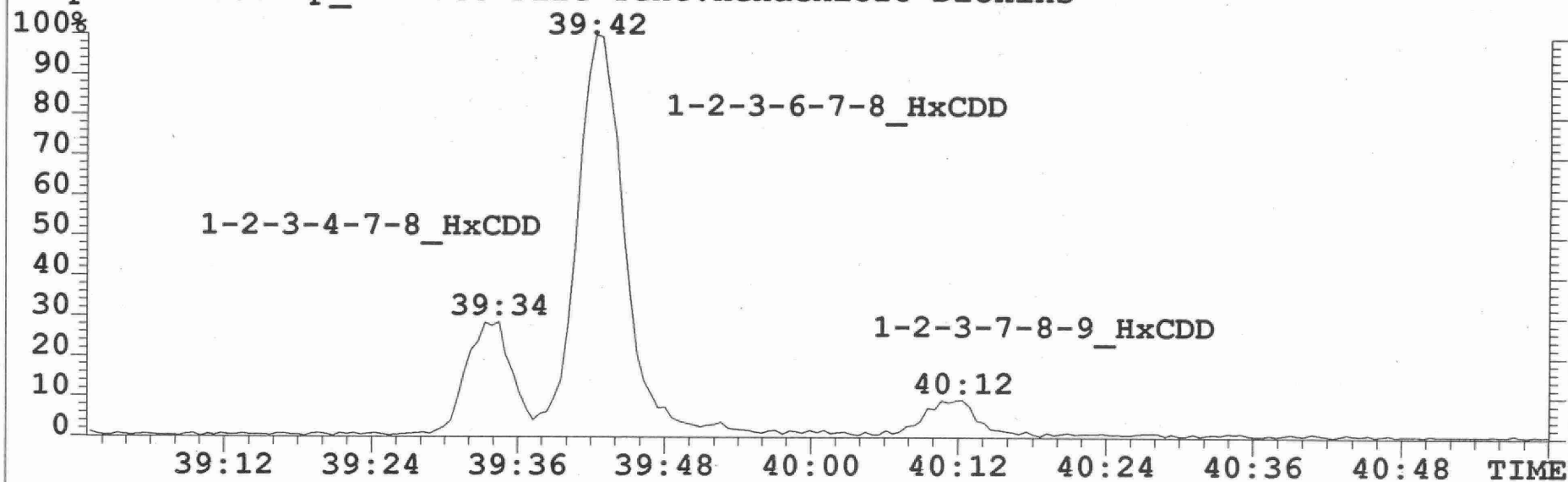


Fig. 3b

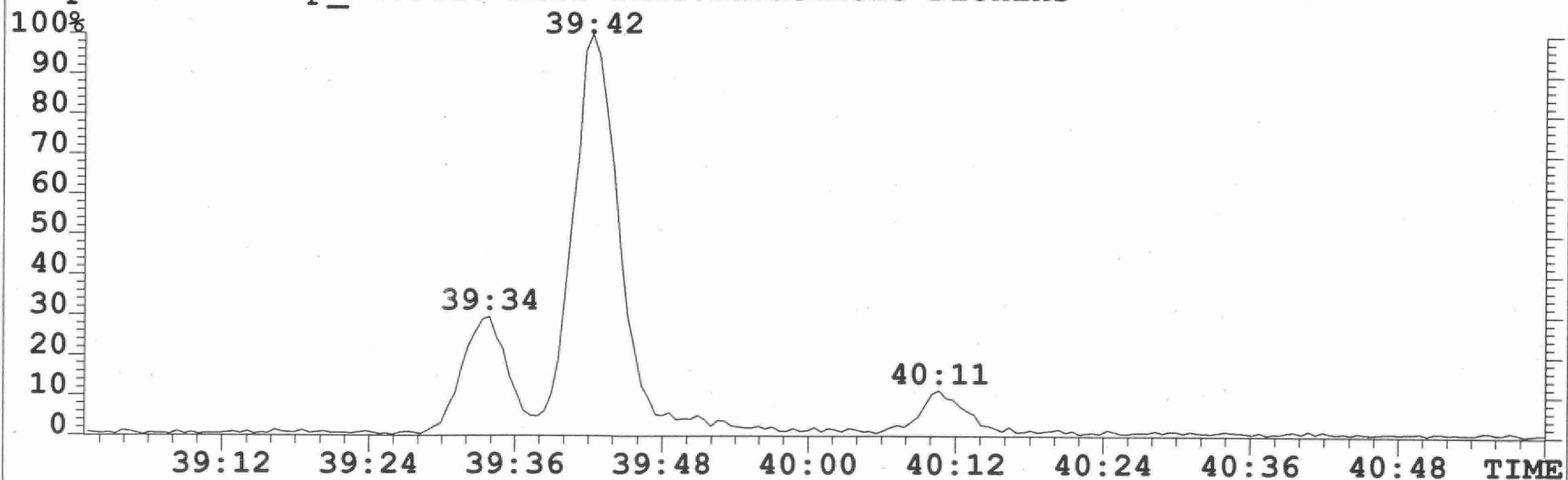
389.8157 Exp:DIOX-6

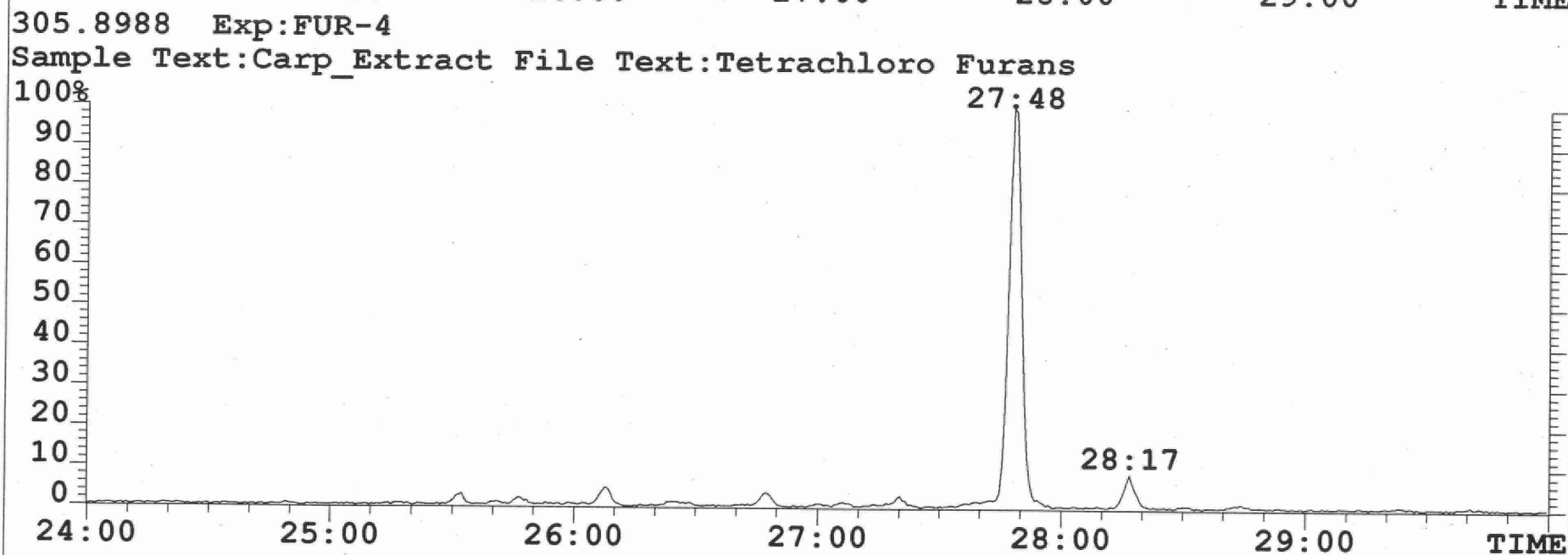
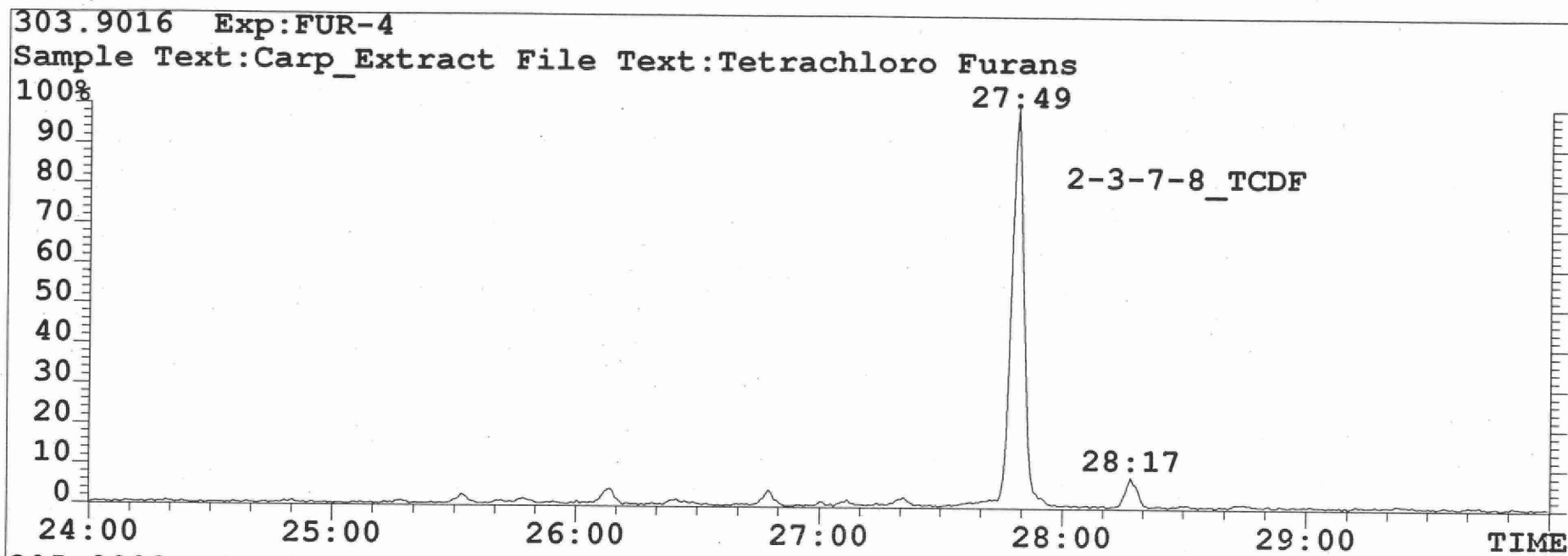
Sample Text:Carp_Extract File Text:Hexachloro Dioxins



391.8128 Exp:DIOX-6

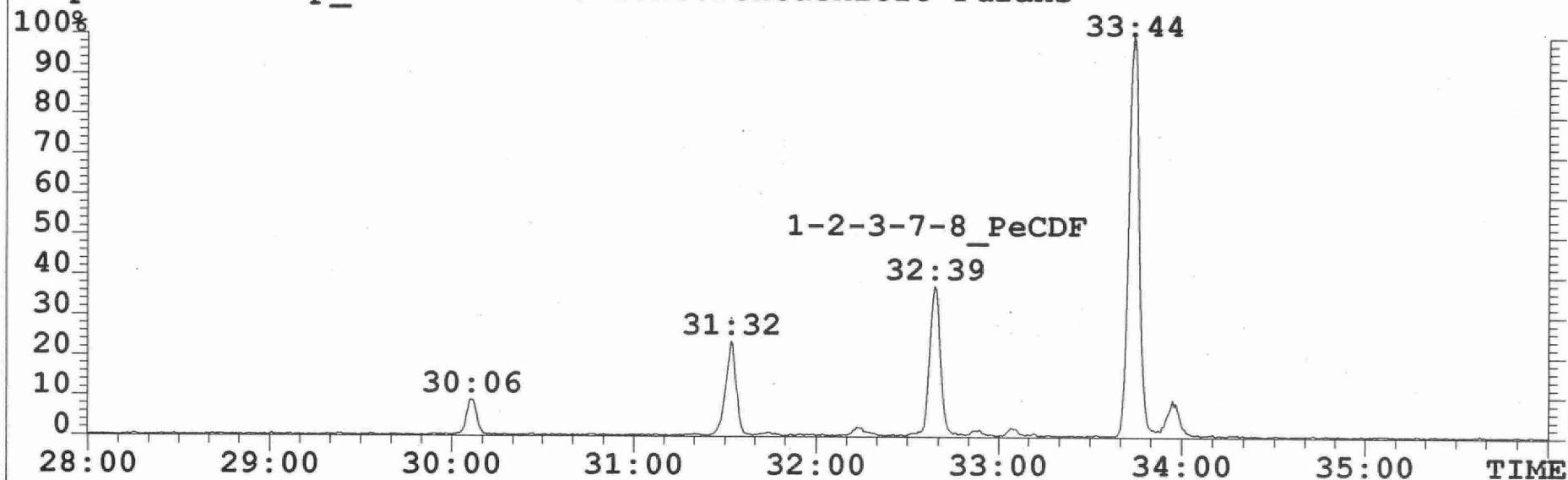
Sample Text:Carp_Extract File Text:Hexachloro Dioxins





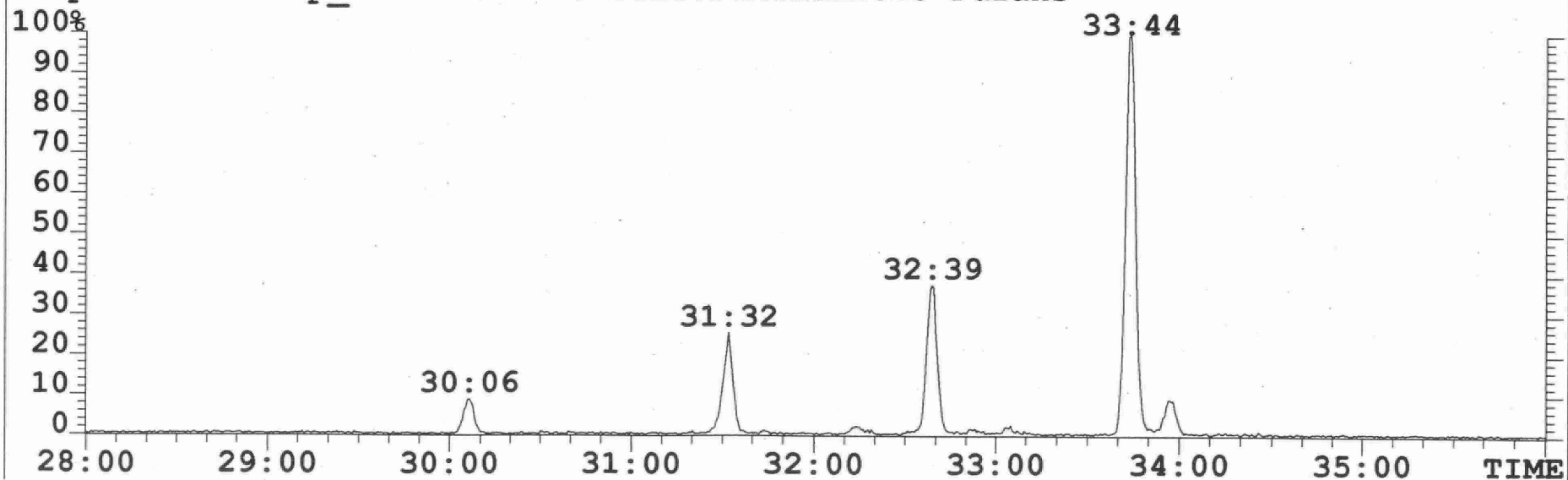
339.8598 Exp:FUR-5

Sample Text:Carp_Extract File Text:Pentachloro Furans



341.8569 Exp:FUR-5

Sample Text:Carp_Extract File Text:Pentachloro Furans



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